THE BEHAVIOR OF EXPLOSIVES AT VERY HIGH TEMPERATURES

Prepared by

JOSEPH WENOGRAD

Approved by: D. V. SICKMAN, Chief
Organic Chemistry Division

ABSTRACT: Recent work at the Naval Ordnance Laboratory has indicated that the impact sensitivities of organic high explosives are related in a simple manner to the velocities of their thermal decomposition reactions at very high temperatures, 300°-1000°C.

It has been possible, by means of a new experimental technique, to measure the time delay to explosion for a series of explosives in this hitherto unexplored range of temperature and reaction rate.

This has been accomplished by loading the explosive into fine hypodermic needle tubing which can then be heated, essentially instantaneously, by a capacitor discharge. The temperature and explosive event are recorded by monitoring the resistance of the tube.

The measured delay times are related to the impact sensitivities of high explosives as sensitive materials are found to explode more rapidly at a given high temperature than less sensitive ones.

Published January 1961

CHEMISTRY RESEARCH DEPARTMENT
U. S. NAVAL ORDNANCE LABORATORY
WHITE OAK, SILVER SPRING, MARYLAND

This report describes a new technique which has been used to investigate the behavior of high explosives in a hitherto unexplored range of temperatures. The work is part of a continuing effort to elucidate the chemical basis of the sensitivity of explosives. The results described herein, while not conclusive, strongly indicate that the chemical kinetic considerations may be of greater importance than any other factor in determining the basic sensitivity of high explosives.

W. D. COLEMAN
Captain, USN
Commander

ALBERT LIGHTBODY
By direction

TABLE OF CONTENTS

ILLUSTRATIONS

TABLE OF CONTENTS
(Cont'd.)

THE BEHAVIOR OF EXPLOSIVES AT VERY HIGH TEMPERATURES

INTRODUCTION

A wide variety of the physical, chemical, and mechanical properties of an explosive determine the absolute value of its impact sensitivity (1,2,3). The author has proposed (4) that of these properties only one, the thermal decomposition velocity at initiation temperature, varies sufficiently among the organic high explosives to account for the differences in relative sensitivity which are observed. The explosives which are most sensitive also prove to be the ones which are least stable at very high temperatures.

High temperature thermal decomposition rates were estimated by extrapolations based on the most reliable values for the Arrhenius parameters of a series of explosives in the available literature. These parameters were obtained in isothermal studies of molten explosives carried out at relatively low temperatures. The direct observation of the behavior of explosives at very high temperatures would avoid reliance on a long extrapolation of low temperature measurements.

In the temperature and time range of interest in impact sensitivity studies, chemical decomposition is so rapid compared to the process of heat transfer as virtually to preclude any isothermal measurements on condensed explosives. Moreover, these temperatures are sufficient to cause the very rapid vaporization of most organic materials and the formation of an insulating layer similar to that supporting a drop of water on a hot skillet. Any experiment designed to ascertain the behavior of explosives in the temperature range 300°-1000°C must apply heat to the material very rapidly, yet hold the material under heavy confinement to prevent vaporization and to contain the material in the hot region.

Another method, apart from decomposition kinetics, which has been used to assess the stability of explosives has been the study of explosion induction times and their temperature dependence (5). Delays do not appear to have been measured for any explosives for times shorter than 0.1 seconds. There have been several attempts to relate these delay times to decomposition kinetics, none of which met with clear success.

This paper describes a new technique which permits the measurement of very brief delay times at high temperatures and considers the application of the measurements to the understanding of the sensitivity of explosives.

EXPERIMENTAL

The major difficulties hindering the observation of explosives subjected to very high temperatures have been overcome by enclosing them in lengths of fine stainless steel hypodermic needle tubing. The low heat capacity and rather high resistivity of the tubes permit them to be electrically heated to high temperatures very quickly. The explosive, being a non-conductor, is unaffected by the ohmic heating but is soon heated by conduction. The small, but significant, temperature coefficient of resistance of the material permits its temperature to be determined through a resistance measurement. The explosion of the contents of a tube can be observed by the change in resistance which it causes. Although the tubes are fine, their geometry and construction are such that they have considerable strength and are able to provide heavy confinement for the explosive. Moreover, the tubing proves to be sufficiently massive that its heat loss to the surrounding air is quite slow in the time scale of these experiments. The situation appears to correspond to the ideal case of an infinite cylinder of explosive at T_0, the surface of which is heated to T_1 at zero time and maintained at this temperature. Thermal explosion equations have been solved with just these boundary conditions, but, as will be seen, the results do not seem to describe these experiments.

The explosives are loaded into No. 28 hypodermic needle tubing fabricated from type 304 stainless steel by the Superior Tube Company, Collegeville, Pennsylvania. This size has an outside diameter of 0.014 inches and an inside diameter of 0.007 inches. The individual experimental tubes are made by soft soldering the tubing to brass binding posts which can be mounted in the circuit with set screws. Before loading, the tubes are annealed to give a constant resistance. This is done by heating them to a cherry red heat by passing about two amps through them. The resistance of the tubes at room temperature (R_0) is determined by measuring the voltage drop across the tubing on passage of a very low current. The tubes are nominally two and one-half inches long between the binding posts and have a resistance of approximately 0.60 ohms.

The resistivity-temperature curve for these tubes was determined by measuring the resistance of tubes heated to known temperatures. This curve is shown in Figure 1. The square points represent temperature measurements made with thermocouples and resistances measured with a Wheatstone bridge. For the round points, the temperatures were measured with an optical pyrometer assuming an emissivity of 0.85, and the resistance values were obtained using a voltmeter and ammeter in a D. C. heating circuit.

In order to fill the tubes, they are prepared with one end open and one end closed*. The open end of the tubing is rested against the bottom of a small beaker containing a small amount of the explosive to be tested. Liquids are placed in a vacuum dessicator and solids in a vacuum oven regulated a few degrees above the melting point. The system including the tubes is then evacuated. Explosive is then forced into the tube by the readmission of air.

Of the explosives tested, only PETN and tetryl are markedly unstable at their melting points. It is felt, however, that the extent of decomposition in the roughly ten minutes they remain at elevated temperature is insufficient to affect these results.

The tubes are studied in the circuit shown schematically in Figure 2. The Thyratron is protected for five minutes after the circuit is energized by the timing motor M and the micro-switch S_2. After five minutes, the relay B is energized and the timing motor is shut off. At the same time, circuit b_1 is opened and b_2 is closed. Closing b_2 lights a pilot light which shows the apparatus is ready for use and the capacitor can be charged. The high voltage power supply, Du Mont, type 263B, cannot put out high voltage if the oscillator coil is shorted out. Thus the capacitor can be charged when relay B is energized and the normally closed b_1 is open. In order to run duplicate shots, the capacitor is charged for a repeated length of time rather than to a specified voltage. This is facilitated by using the Gralab timer T which energizes relay C for a preset interval. After the capacitor has been charged it is discharged by closing the circuit through a_1. This is done with a mercury wetted contact in mercury relay A which completes the circuit very rapidly and without chatter. Subsequent D. C. measurements of the explosion temperature and time can then be made.

---

* Tubing can be cut without collapsing the walls if a sharp, scissors type of wire cutter is used. Diagonal or side cutters do a good job of sealing off the end of the tubing.

A simplified diagram of the D. C. measuring circuit is shown in Figure 3. The capacitor discharges its energy through all three branches of this circuit, but because of the lower resistance of the branch $R_1 + R_2$, most of the current flows through this path. When the capacitor has finished discharging, the high voltage pulser represents an open circuit and only the simple Wheatstone bridge powered by E_b through R_A remains.

The unbalance voltage of the bridge, which is related to the temperature of the tube under test, is recorded on a type 535 Tektronix oscilloscope with a type D plug-in unit and a Du Mont type 2614 oscillographic record camera. Usable sweep rates for these experiments vary from 20 microseconds/cm to 10 milliseconds/cm. The value of E is measured on the oscilloscope using a gain of 10 mV/cm making the vertical range of the 6 cm face 60 mV. Since the voltage measured may go as high as 400 mV, the bottom line on the 6 cm graticule is set at some voltage slightly below the reading expected from the known energy input. This is done by a known voltage bias from a simple D.C. power supply made with a mercury battery, a 10 turn "helipot" and a calibrated voltmeter.

The resistance of the tube under test can be computed from the bridge output voltage E and the known parameters of the circuit using the expression

$$R_1 = \frac{25E_BR_2 + ER_AR_2 + 50ER_2 + 50ER_A}{25E_B - ER_A - 50E} \quad (1)$$

The scope is triggered internally by the capacitor discharge. The discharge heats the tube close to its final temperature in about 20 microseconds. After the circuit has settled down, the value of E can be used to compute the temperature of the wire. When the material in the tube explodes, the tube is ruptured and its resistance changes in an abrupt manner which is clearly visible on the trace. The temperature just before this abrupt change is taken as the explosion temperature. The explosion time is the time at which the sharp break in the trace occurs minus the 20 microsecond heating time.

A representative oscillographic record is shown in Figure 4. This was obtained from a shot of TNETB in No. 28 tubing and illustrates the procedure used.

4

RESULTS AND DISCUSSION

A series of explosives and liquid propellant ingredients have been studied by the method described above.

For most explosives, a plot of the logarithm of the time delay as a function of the reciprocal of the absolute temperature is linear over a considerable range of temperatures. That is, the materials conform to the expression:

$$\tau = A \exp(B/RT) \qquad (2)$$

where τ is the time delay, T is the absolute temperature of the tube at the time of explosion, and A and B are constants.

The explosives studied have been subjected to temperatures in the range 260°C to 1100°C and time delays varying between 50 milliseconds and 50 microseconds have been measured. The lower measurable time limit is determined by the duration of the capacitor discharge pulse. The measurement of times longer than than 50 milliseconds is complicated by the cooling of the tubing and by the evaporation of the explosive out of the end of the tubes.

The results for the materials studied are summarized in Figures 5 to 12.

The results for two typical high explosives, 2,4,6-trinitrotoluene (TNT) and pentaerythritol tetranitrate (PETN) are shown in Figure 5. Despite the scatter, the results are fairly linear over the wide ranges of temperatures studied. Figure 6 shows the results for 1,3,5-trinitrobenzene (TNB), di β-nitroxyethyl nitramine (DINA), and nitroglycerine (NG). Again, the results appear linear over the range of study. A similar graph for N-methyltrinitrophenylnitramine (tetryl) is shown in Figure 7.

An unexpected phenomenon has come to light in the course of experiments with three explosives containing the terminal trinitromethyl group. This is illustrated in Figure 8, which shows experimental points for 2,2-dinitropropyl 4,4,4-trinitrobutyrate (DNPTB) in No. 28 hypodermic needle tubing. There is a definite inflection with comparatively little scatter in the middle of the range of accurate measurements. A similar but more pronounced inflection has been observed for 2,2,2-trinitroethyl-4,4,4-trinitrobutyrate (TNETB). In fact, in this case, there is evidence of an upward turn in the explosion delay time above the inflection temperature.

The time temperature plot for TNETB is shown in Figure 9. Bis-(2,2,2-trinitroethyl) nitramine (BTNEN) gave evidence of a similar behavior but with faster reaction times and considerably more scatter.

The reasons for this behavior are at present obscure. However, experiments in which the size of the hypodermic needle tubing was varied showed drastic changes in the high temperature portions of the curves. When finer tubing was used the inflections were found to be less pronounced although the low temperature behavior and the points of inflection remained unchanged. These facts suggest that the inflections are caused by the experiment rather than by any change in the decomposition mechanism of these materials at elevated temperatures.

Several liquid propellant ingredients have also been studied by this technique. Figure 10 shows the results for ethyl nitrate and nitroethane. There is considerable scatter in the ethyl nitrate points and a suggestion of curvature in the case of nitroethane. Figure 11 shows the results for n-propyl nitrate and nitromethane.

The slopes of these delay time-reciprocal temperature curves may be regarded as adiabatic activation energies for the compounds studied. These results are similar to those of Henkin and McGill (5) who worked at considerably lower temperatures. The experimental configuration described in this report appears to correspond to the situation where an infinite cylinder of explosive is at some temperature T_0 and its surface is instantaneously raised to and maintained at some higher temperature. The equation which Frank-Kamenetskii (6) proposed to describe the onset of thermal explosions has been integrated with boundary conditions corresponding to this problem both by Cook (7) and by Zinn and Mader (8). Their calculations agree that these adiabatic activation energies should correspond with the activation energies of the heat producing thermal decomposition reactions.

The observed slopes and intercepts, A and B values in equation 2, are shown in Tables I and II. The values describing the polynitroaliphatic explosives are taken from the low temperature portions of their curves. Because of the curvature, limiting lower temperature slopes are quoted for nitromethane and nitroethane. Also included in Table I are Arrhenius activation energies for these compounds as obtained from isothermal decomposition studies on the liquid explosives at lower temperatures (9-13). The decomposition of the four liquid propellant ingredients do not appear to have been

studied in the liquid phase. It can be seen that the adiabatic activation energies are much lower than those obtained from isothermal studies.

The failure of these two sets of data to show the predicted correspondence might conceivably be due to some inaccuracy in the experimental procedure described herein, although this is not likely. It is also possible that the mathematical model used in the integrations does not adequately describe the physical situation being considered. Some of the approximations regarding the constancy of such variables as heat of reaction and thermal conductivity might be too drastic. It must be remembered, however, that the most drastic assumption is that of a unimolecular, zero order, exothermic decomposition reaction. The chemical process must be more complex and it is possible that this complex reaction does indeed have the measured temperature dependence in the range of temperatures under consideration.

The proposal that the high temperature decomposition velocity is the most important factor determining the relative impact sensitivity of an explosive can now be tested. The hot tube experiments employ a purely thermal initiation process and none of the mechanical properties of the explosive can influence the result. If a scale of sensitivities based on the hot tube experiments can be established which corresponds with the scale observed in impact testing, it would imply that the effect of differences in mechanical properties on relative impact heights might be regarded as being of lesser importance.

One would expect more sensitive explosives to explode more rapidly at a given high temperature than less sensitive ones. Thus, in a graph such as Figure 13 it would be expected that the sensitive explosives would tend towards the lower right-hand corner. In going towards the upper left, lines representing successively less sensitive materials would be intercepted. The impact sensitivities of the explosives represented in Figure 13 as measured by the Explosives Research Laboratory impact test as used at the Naval Ordnance Laboratory, are reported in Table I. It can be seen that the more sensitive materials do indeed explode more rapidly and at lower temperatures than insensitive ones.

A similar relation applies to the sensitivity of the liquids. Their sensitivities as measured by Olin-Matheson drop weight test (15) are shown in Table II. The scale of sensitivities is quite compressed at the sensitive end.

The time temperature curves for the four liquid propellant ingredients are shown in Figure 14. It is seen that again the more sensitive materials explode more rapidly and at lower temperatures than the less sensitive ones.

In an impact experiment there is a rather short period of time during which the explosive is heavily confined. In order for an impact explosion to occur, the initiation of the reaction must occur before the pressure is released by the rebound of the tools. Warner and Smith (14) have measured the duration of impact by studying the variation with time of the pressure in the anvil of an impact machine similar to that employed at the Naval Ordnance Laboratory. They found that the anvil was under pressure for about 250 microseconds although the presence of a sample complicated the picture somewhat. The ease of initiating impact explosions can thus be related to the ease of forming centers capable of build-up in 250 microseconds or less. For each explosive there is a temperature above which initiation in hot tubes occurs within this interval. These critical temperatures are recorded in Table I.

A plot of these critical temperatures as a function of Naval Ordnance Laboratory impact sensitivities is shown in Figure 15. With the exception of the values for tetryl and DNPTB, the data are seen to fit a smooth curve fairly well. Both of the explosives which deviate have low slopes which render their critical temperatures particularly sensitive to the selection of the confinement interval. The agreement which exists serves to corroborate the view that the relative sensitivities of organic high explosives are determined largely by their thermal decomposition rates at high temperatures.

ACKNOWLEDGMENT

BIBLIOGRAPHY

(1) F. P. Bowden and A. D. Yoffe, "Initiation and Growth of Explosions in Liquids and Solids", University Press, Cambridge, 1952.

(2) E. K. Rideal and A. J. B. Robertson, Proc. Roy. Soc., A 195, 135 (1948).

(3) J. L. Copp, S. E. Napier, T. Nash, W. J. Powell, H. Shelley, A. R. Ubbelohde, and P. Woodword, Phil. Trans. Roy. Soc. A 241, 197 (1948).

(4) J. Wenograd, NavOrd Report (NOL) 5730, "The Correlation of the Impact Sensitivity of Organic High Explosives with their Thermal Decomposition Rates", 30 Sept 1957.

(5) H. Henkin and R. McGill, Ind. Eng. Chem. 44, 1391, (1952).

(6) D. A. Frank-Kamenetskii, Acta. Physiochim, U.R.S.S. 10, 365 (1939).

(7) G. B. Cook, Proc. Roy. Soc. A 246, 154 (1958).

(8) J. Zinn and C. L. Mader, J. App. Phys. 31, 323 (1960).

(9) A. J. B. Robertson, J. Soc. Chem. Ind. 67, 221 (1948).

(10) J. Wenograd, unpublished results.

(11) A. D. Little, Inc. Private Communication, April 1954.

(12) A. J. B. Robertson, Trans. Faraday Soc. 44, 677 (1948).

(13) M. A. Cook and M. T. Abegg, Ind. Eng. Chem., 48, 1090 (1956).

(14) L. C. Smith and R. F. Warner, Los Alamos Scientific Laboratory, Private Communication.

(15) C. F. Turner and J. E. Regan, p. 187, First Meeting of JANAF Liquid Propellant Group, Liquid Propellant Information Agency, Johns Hopkins Applied Physics Laboratory, 1959.

TABLE I

Explosive	Impact Sensitivity 50% ht. cm. 2.5 Kg. weight	A	$B \times 10^{-3}$	Literature Values for E* kcal/mole	Critical Temperature for Explosion in 250 Microsec. °C
Nitroglycerine	4-8	-10.8	21.8	48.0 (10)	390
PETN	13	- 9.9	20.4	47.0 (10)	430
BTNEN	11	- 9.8*	20.2*	42.5 (11)	440*
TNETB	18	- 9.5*	21.0*	43.4 (12)	500*
DINA	30	- 9.3	20.5	49.8 (11)	510
DNPTB	32	-11.9*	28.4*	-	830**
Tetryl	36	- 5.7	11.1	38.4 (13)	880
Trinitrobenzene	100	- 7.9	26.3	-	1060
TNT	160	- 6.6	18.0	43.3 (14)	1040

* Values refer to low temperature portion of curve.
** Values refer to high temperature portion of curve.

TABLE II

Liquid Propellant Ingredient	Drop Weight Sensitivity by Olin-Matheson Test (15)	A	$Bx10^{-3}$
Ethyl Nitrate	1.9	- 6.9	13.4
n-Propyl Nitrate	15.7	- 6.7	14.7
Nitromethane	67.4	-11.1	35.7
Nitroethane	does not fire	- 8.0	23.4
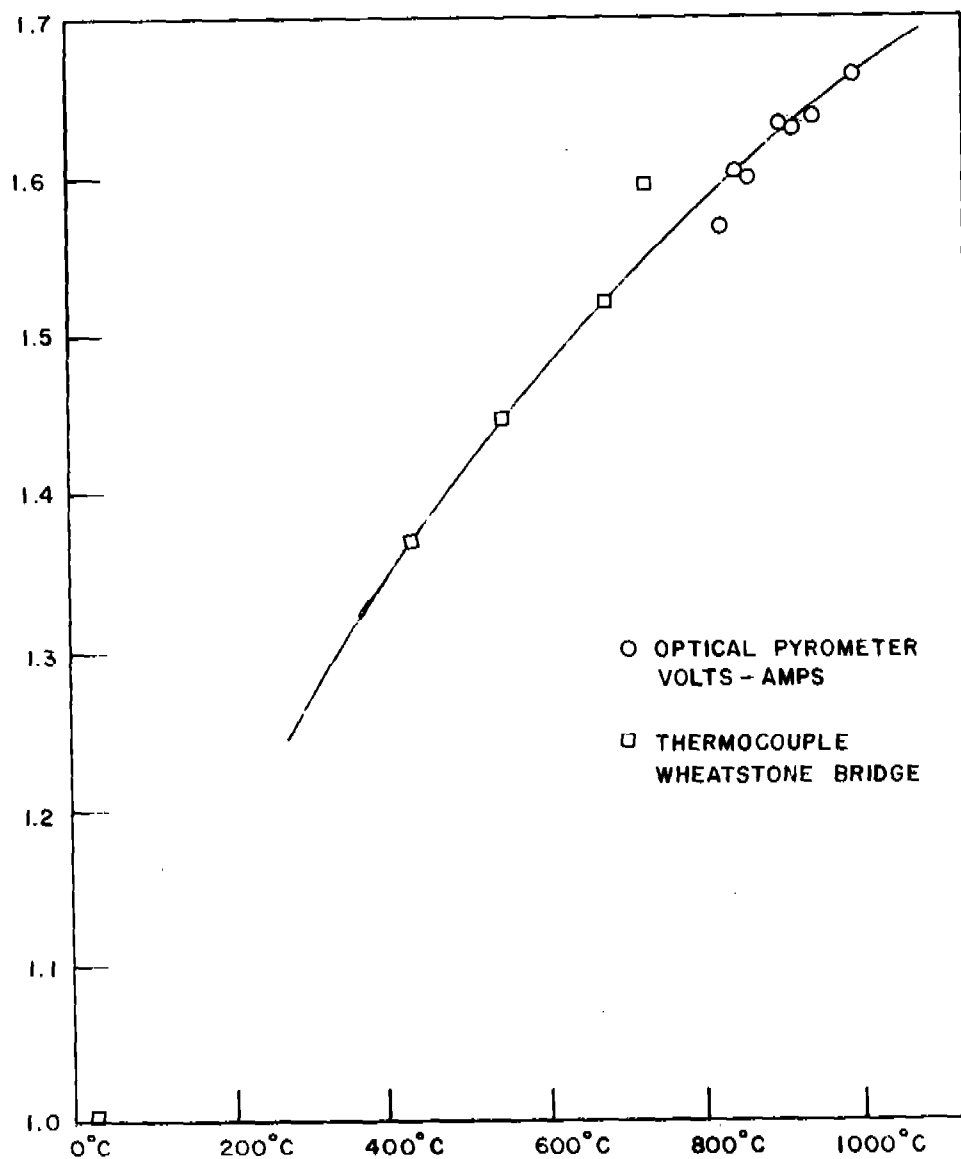
FIG. I RESISTANCE TEMPERATURE CURVE
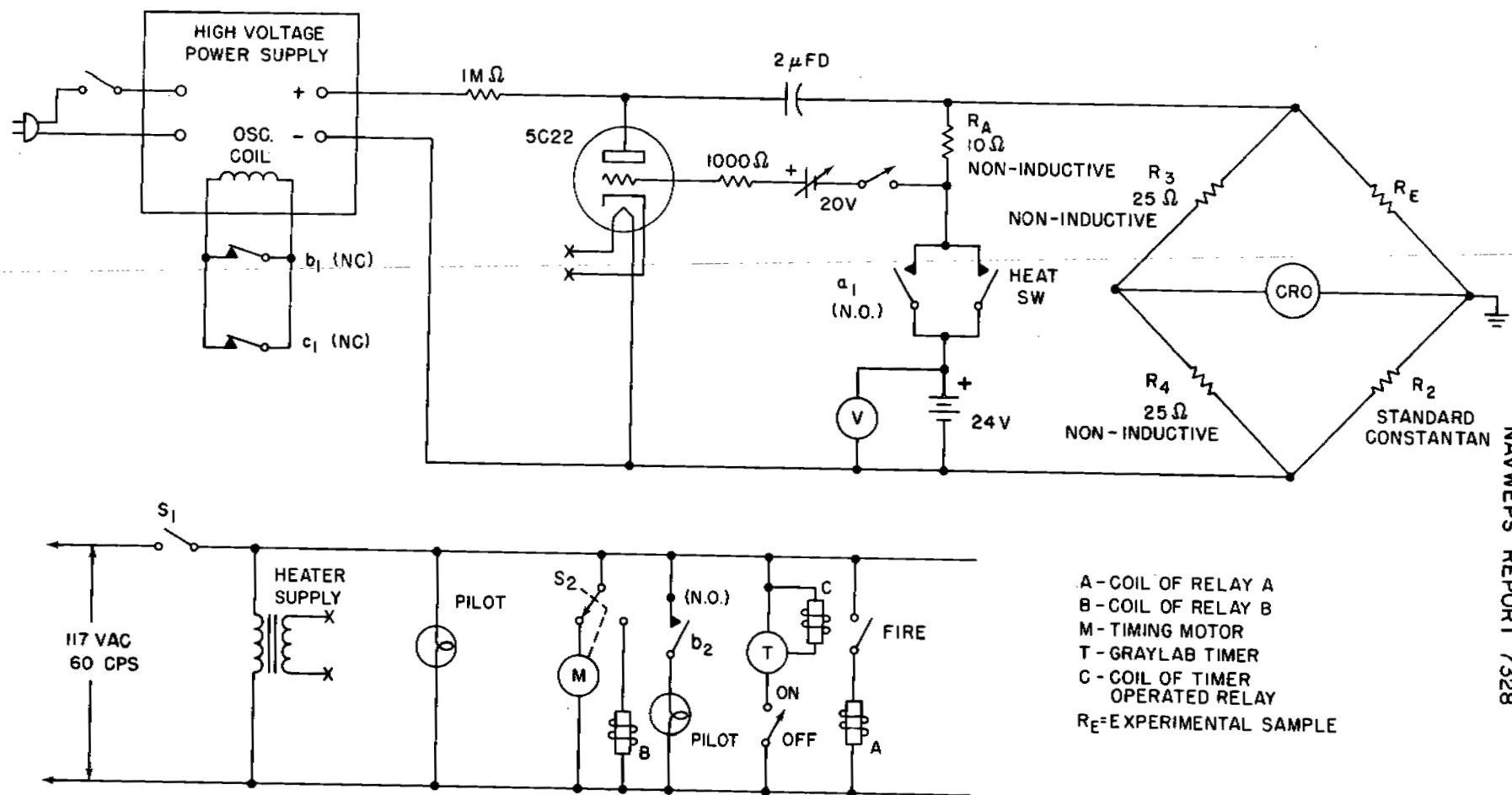
FIG. 2 CIRCUIT FOR OBSERVING BEHAVIOR OF EXPLOSIVES AT VERY HIGH TEMPERATURES
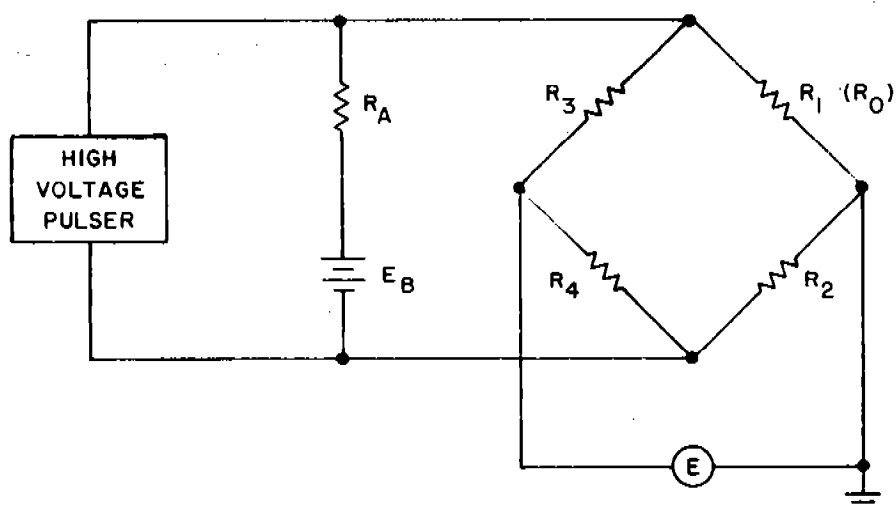
E_B = 24 VOLT STORAGE BATTERY

R_A = 10Ω 250W, NON INDUCTIVE

R_0 = STEEL TUBE (ROOM TEMP)

R_1 = STEEL TUBE (HOT)

E = BRIDGE OUTPUT

FIG. 3 D.C. CIRCUIT
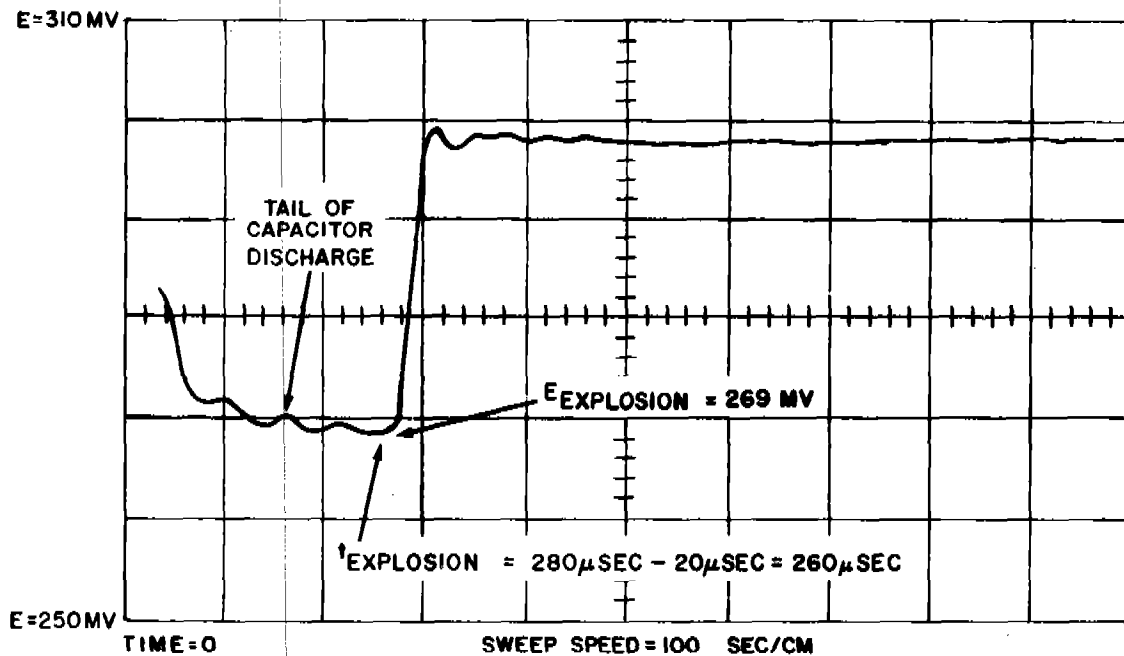
FIG. 4 OSCILLOSCOPE RECORD OF EXPLOSION
OF TNETB SAMPLE IN NO. 28 TUBING
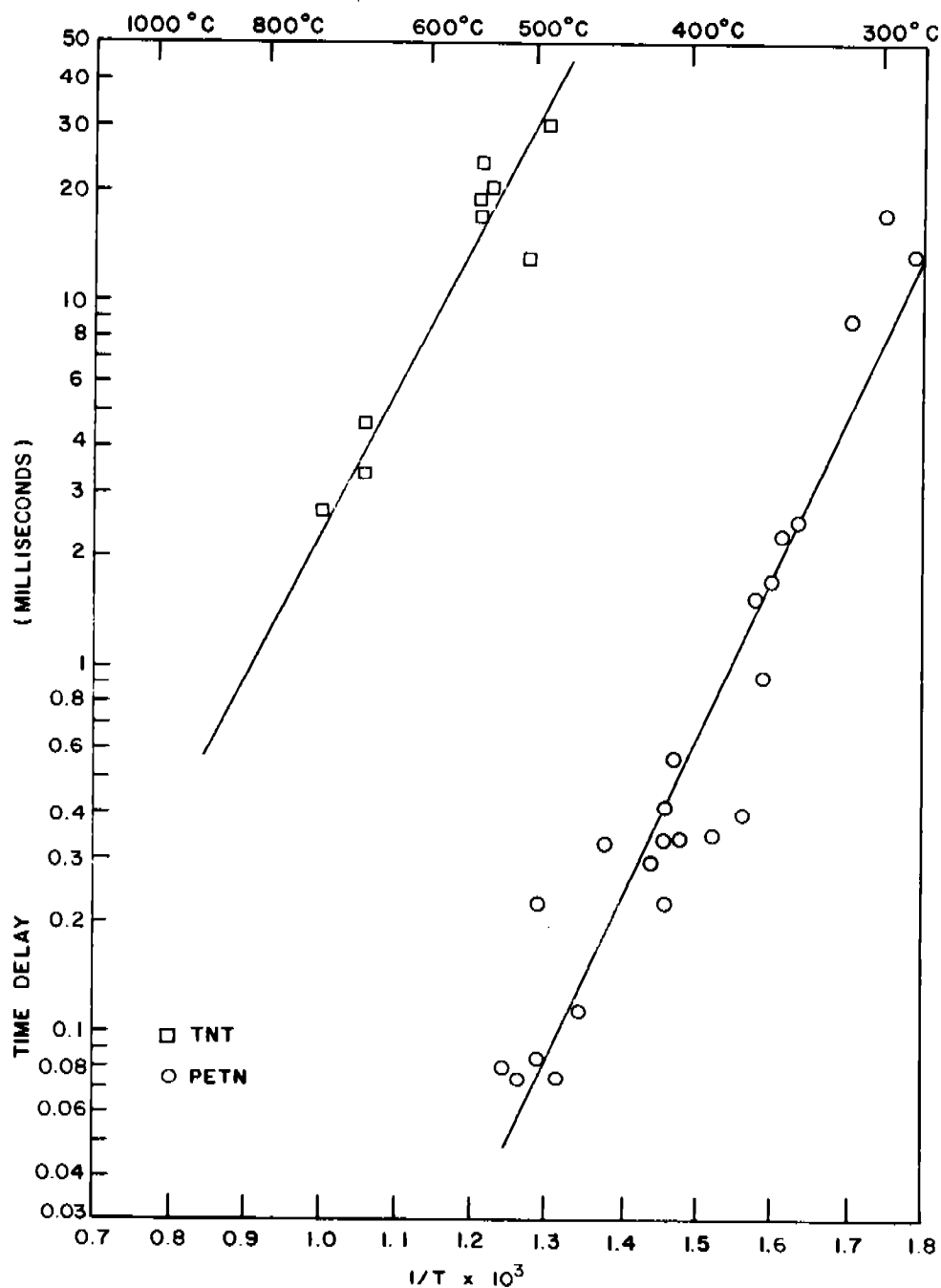
FIG. 5 PETN AND TNT
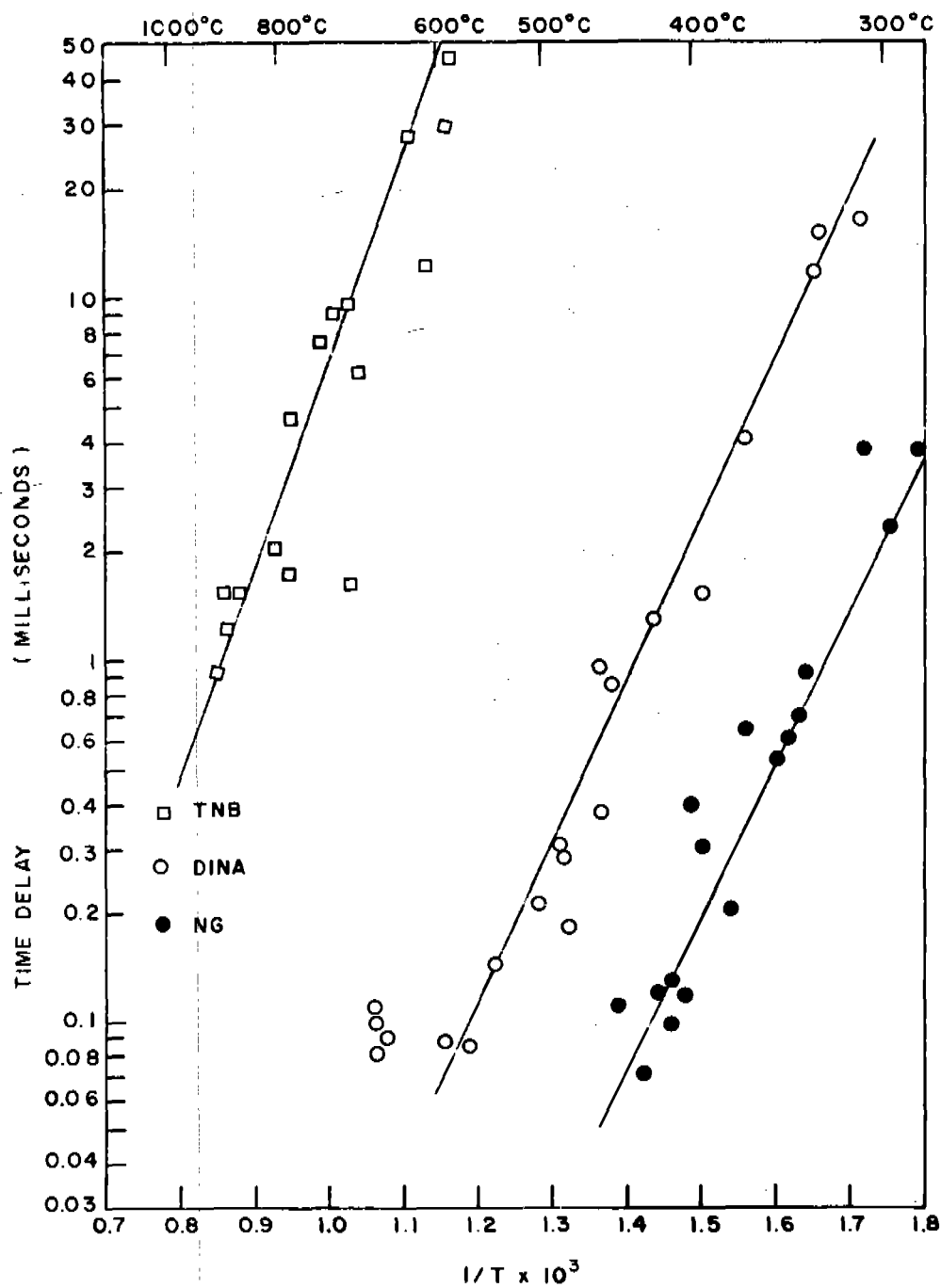
FIG. 6   TNB, DINA AND NG
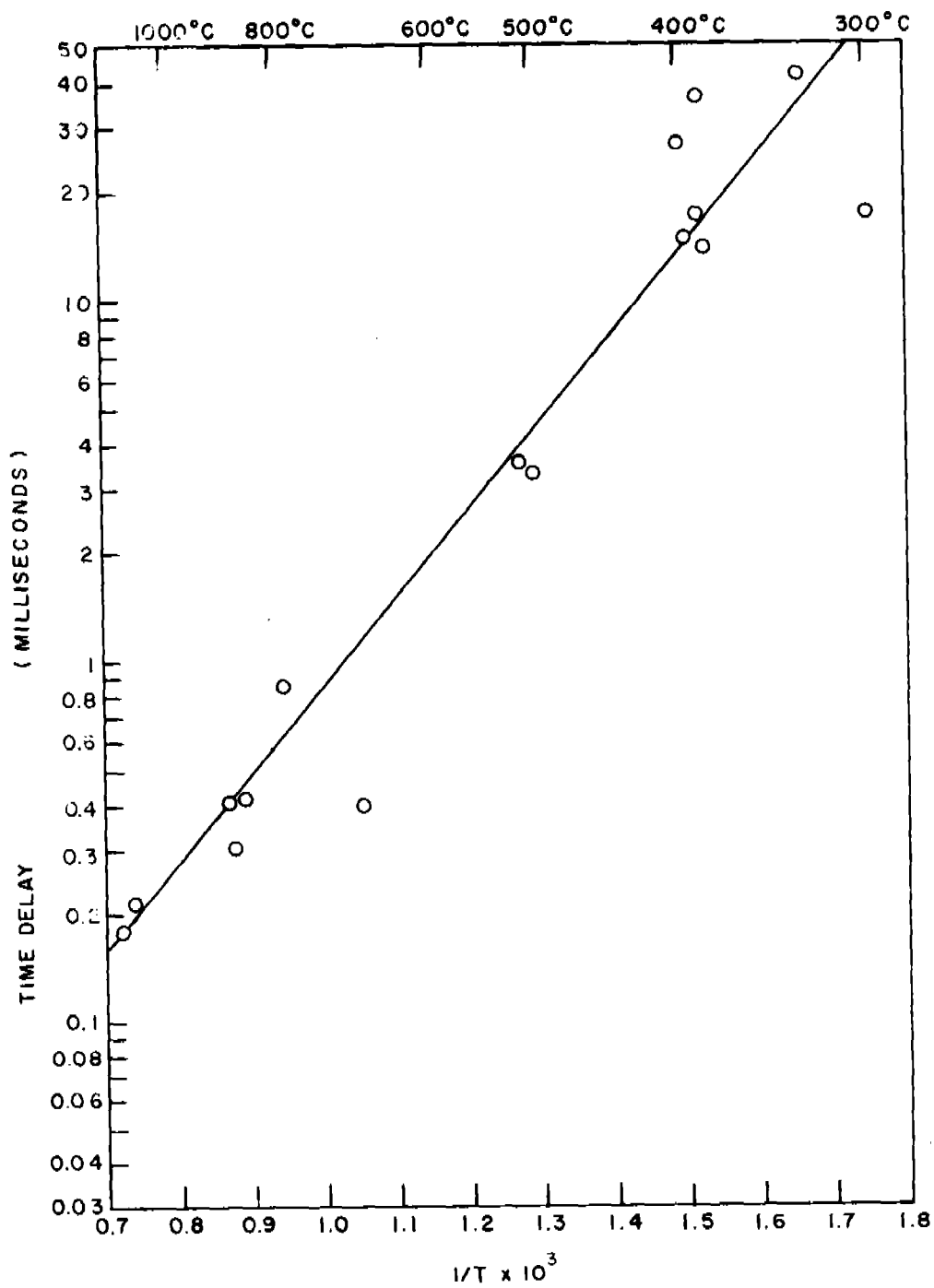
FIG. 7   TETRYL
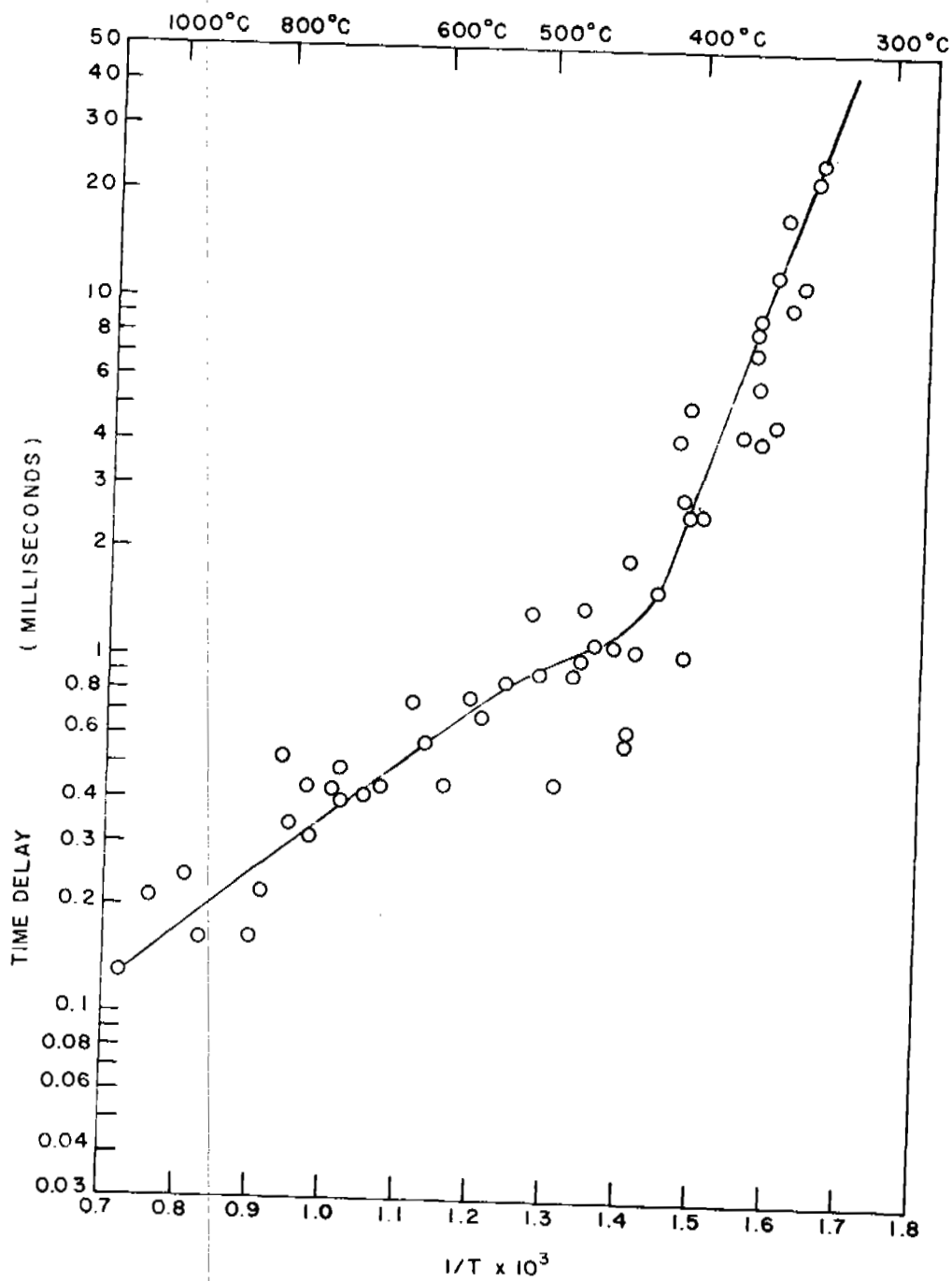
FIG. 8 DNPTB
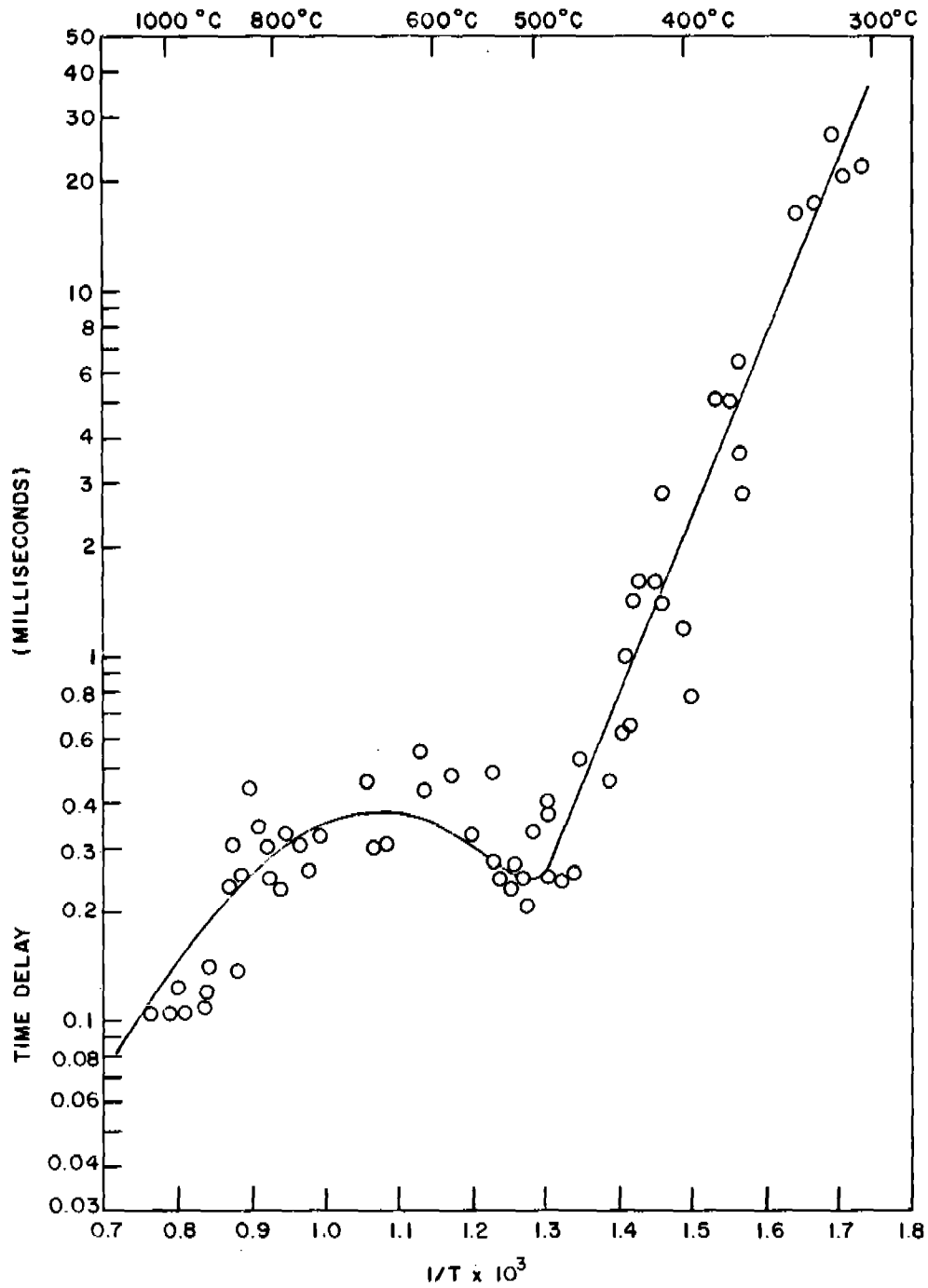
FIG. 9 TNETB
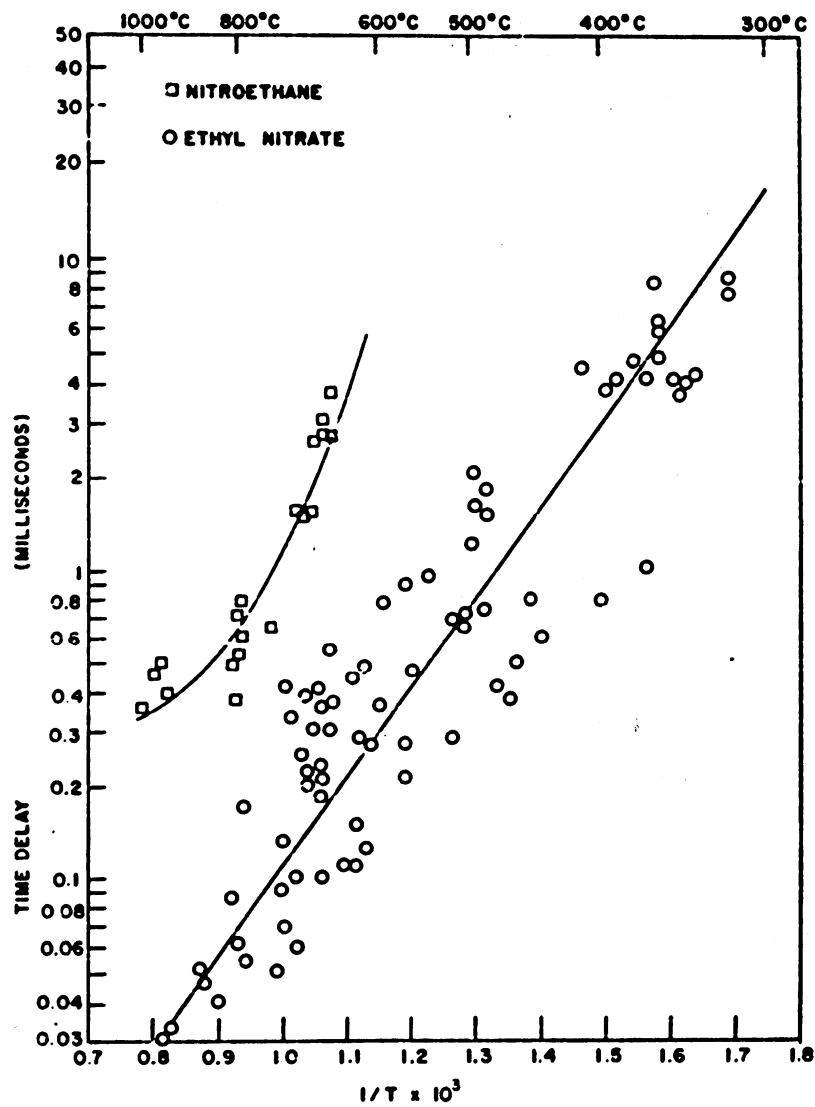
FIG. 10 ETHYL NITRATE AND NITROETHANE
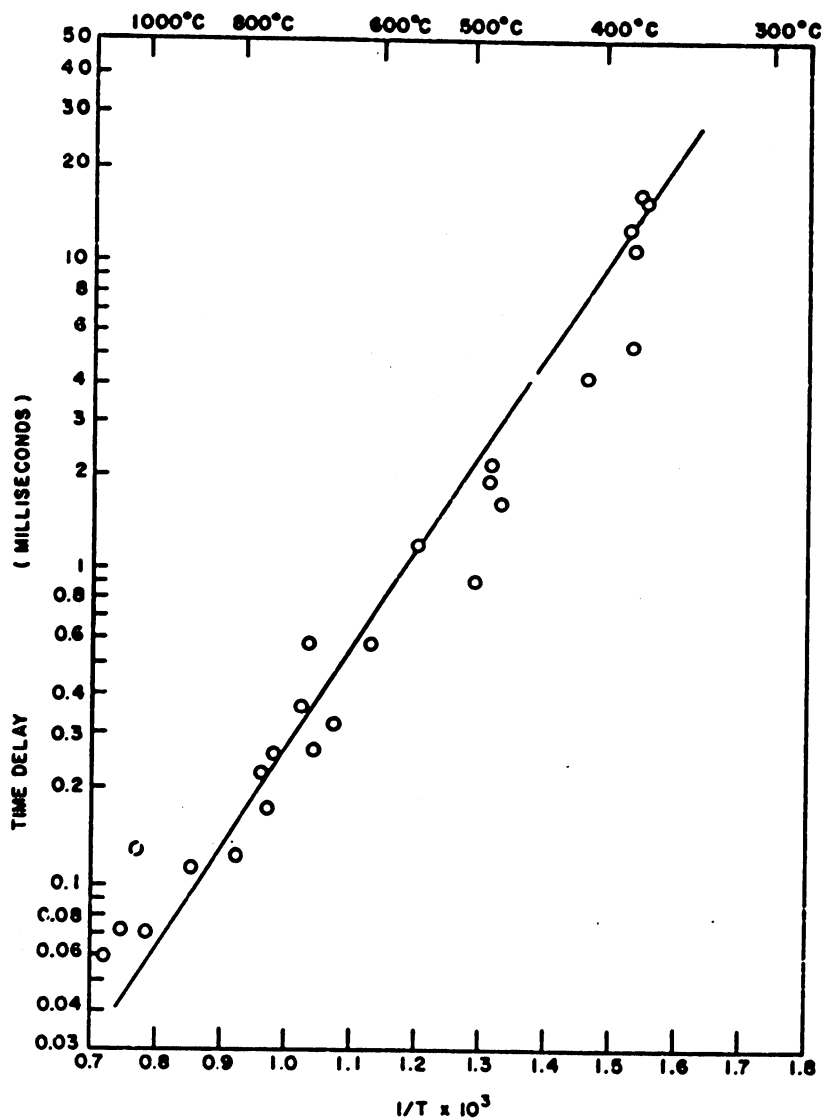
FIG. II N-PROPYL NITRATE
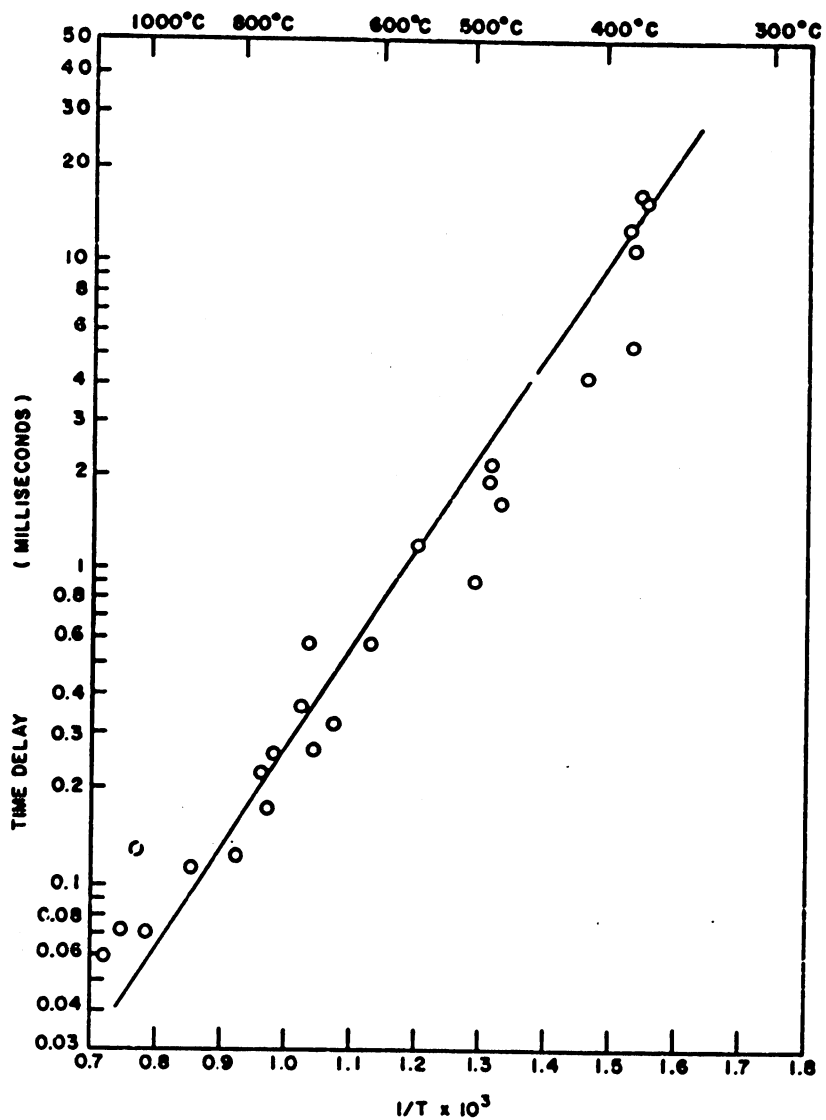
FIG. II N-PROPYL NITRATE
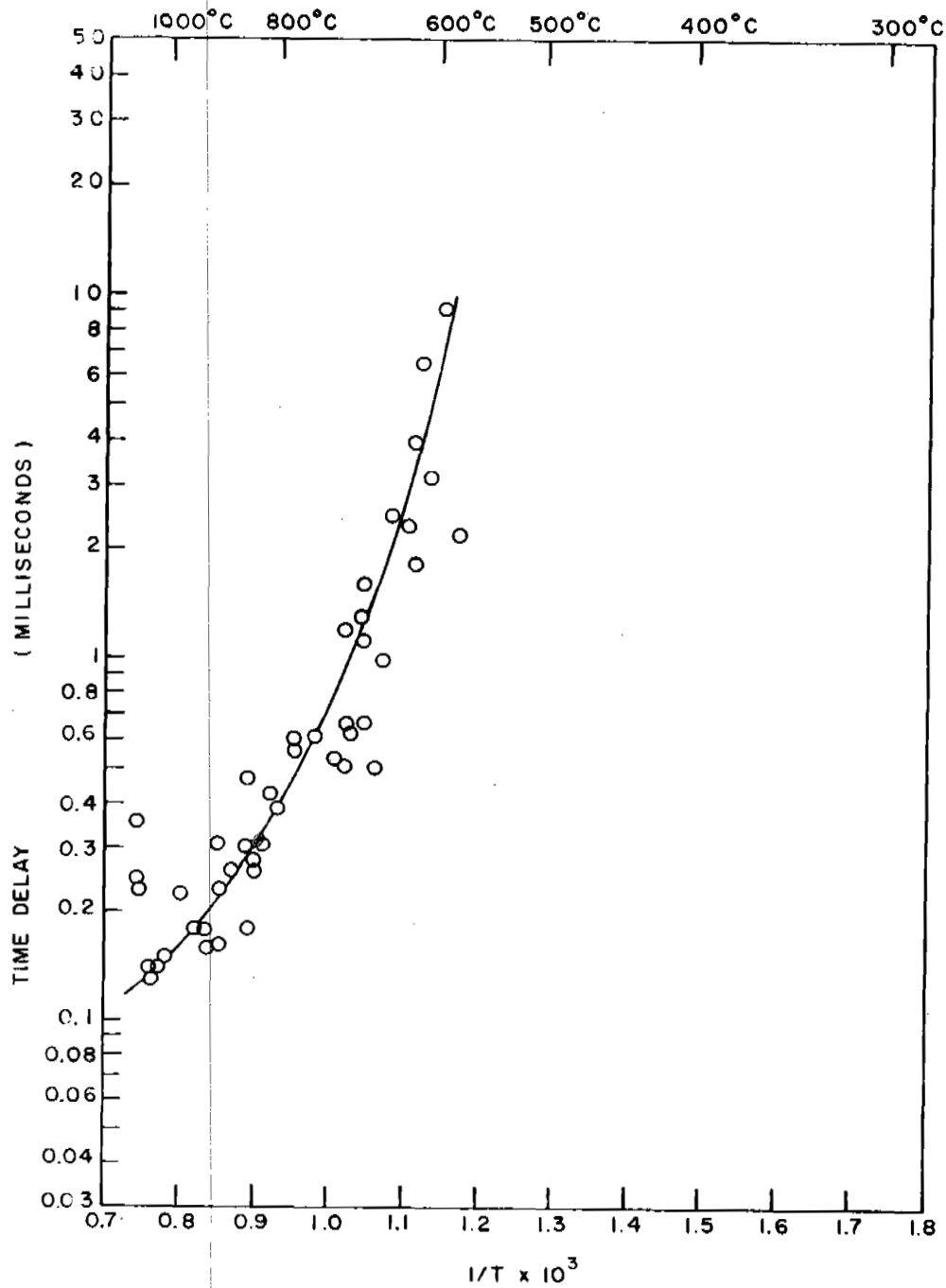
FIG. 12   NITROMETHANE
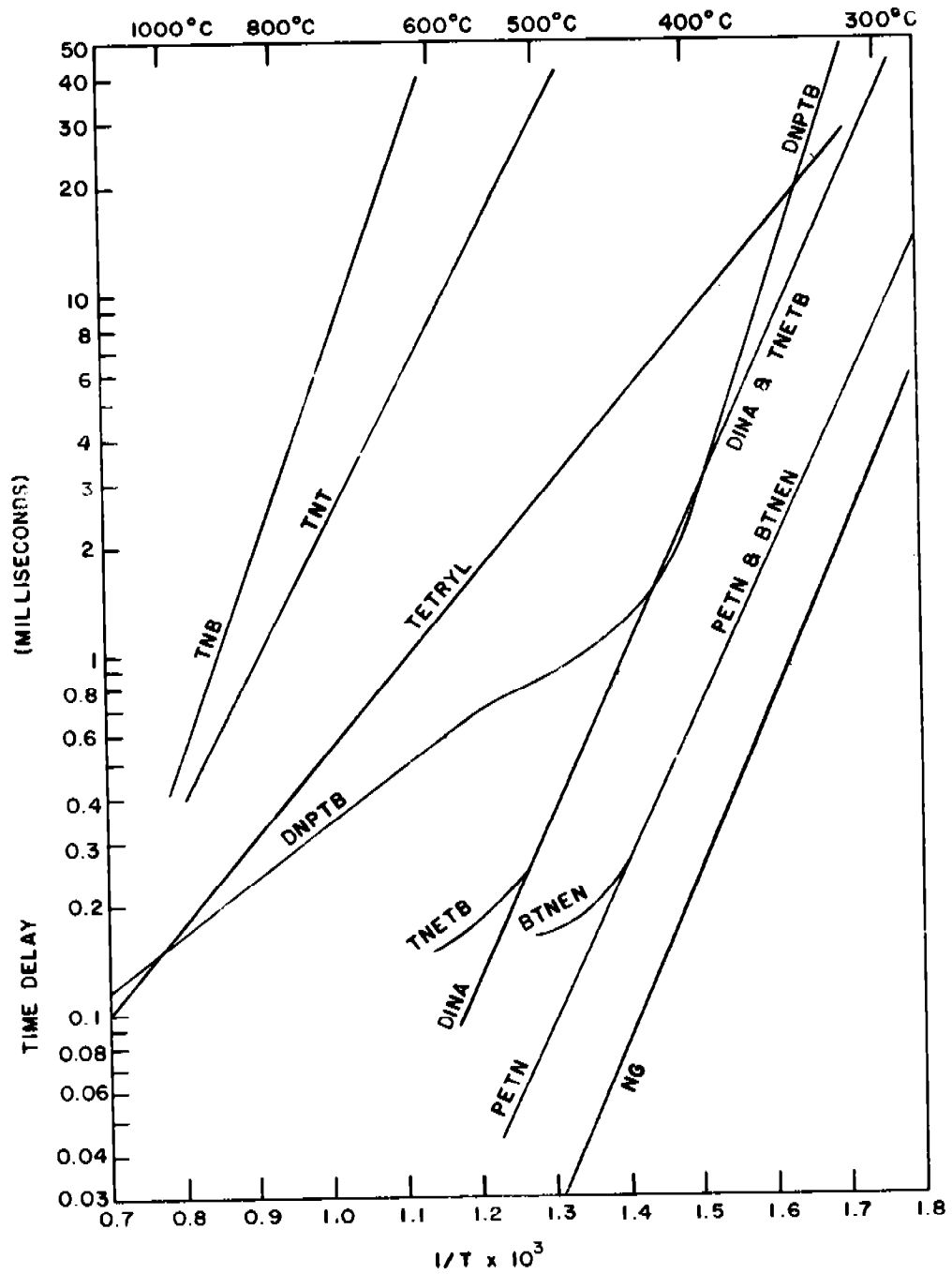
FIG 13 EXPLOSIVES
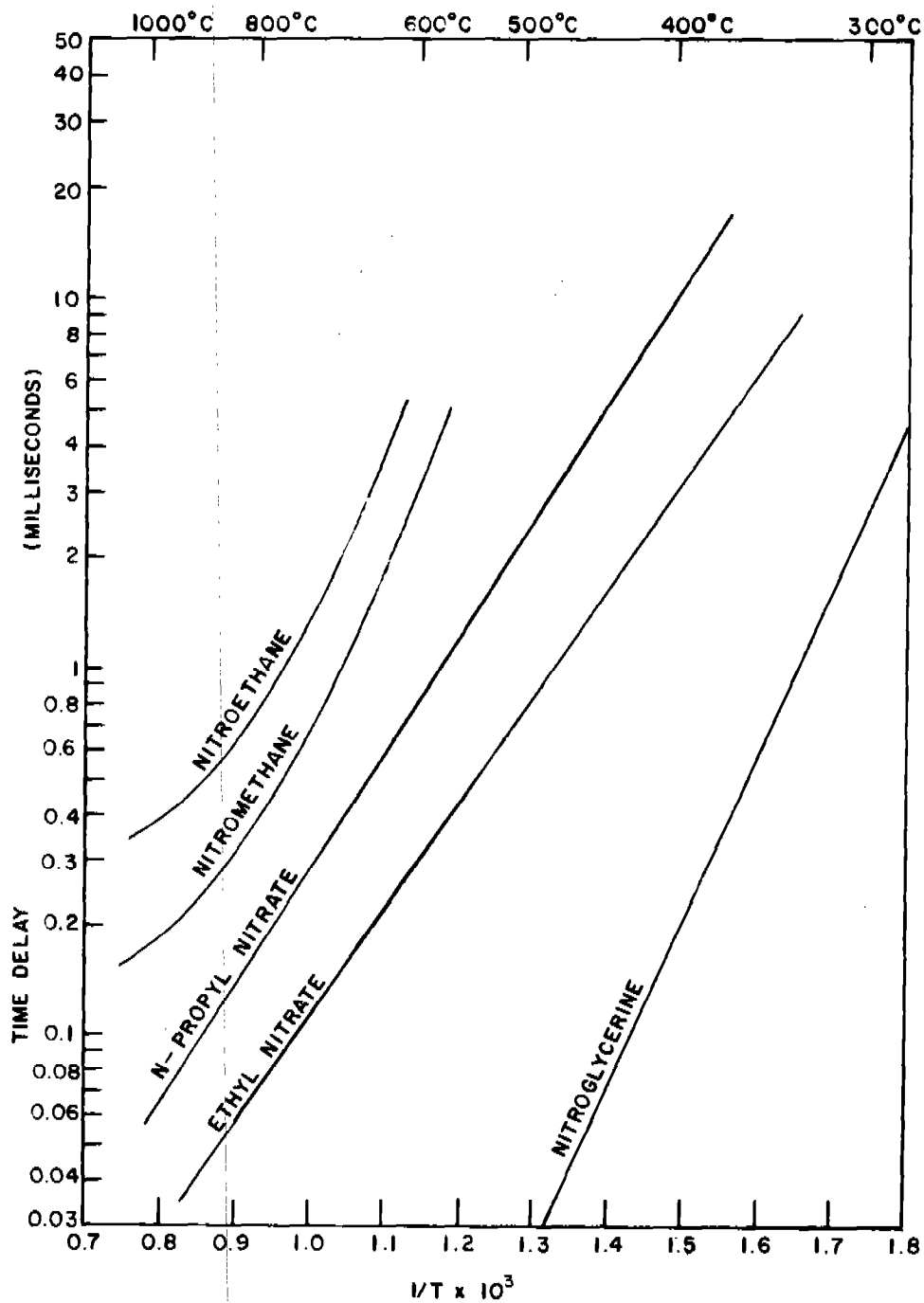
FIG. 14 LIQUIDS
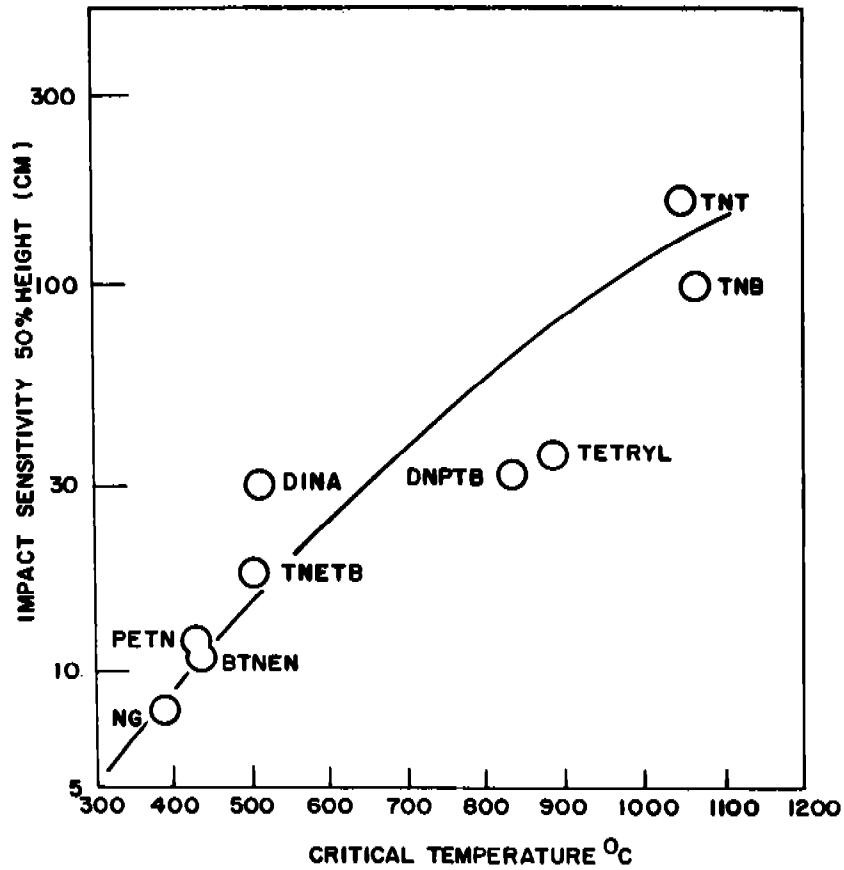
FIG. 15 IMPACT SENSISTIVITY VS CRITICAL
TEMPERATURE FOR EXPLOSION IN 250μSEC

DISTRIBUTION
(Cont'd.)

No. of
Copies

Aerojet-General Corporation, Azusa, California
   Attn: Dr. J. R. Fisher 1
Aerojet-General Corporation, P. O. Box 1947,
   Sacramento, California
   Attn: Dr. Marvin Gold 1
Liquid Propellant Information Agency
   Distribution List 115

Naval Ordnance Laboratory, White Oak, Md.
  (NAVWEPS report 7328)
  THE BEHAVIOR OF EXPLOSIVES AT VERY HIGH
TEMPERATURES, by Joseph Wenograd. 14 Oct.
1960. 8p. tables. Project RUU03E017/212-
1/WF008-10-004.   UNCLASSIFIED
  Recent work at the Naval Ordnance Laboratory
has indicated that the impact sensitivities of
organic high explosives are related in a sim-
ple manner to the velociities of their thermal
decomposition reactions at very high tempera-
tures, 300°-1000°C.
  It has been possible, by means of a new
experimental technique, to measure the time
delay to explosion for a series of explosives
in this hitherto unexplored range of tempera-
ture and reaction rate.
  This has been accomplished by loading the
explosive into fine hypodermic needle tubing
which can then be heated, essentially instan-
taneously, by a capacitor discharge. The

(over)

1. Explosives,
   High – High
   temperatures
2. Explosives,
   High –
   Sensitivity
3. Explosives,
   High – Impact
4. Explosives,
   High –
   Decomposition
I. Title
II. Wenograd,
   Joseph
III. Project

temperature and explosive event are recorded
by monitoring the resistance of the tube.
   The measured delay times are related to the
impact sensitivities of high explosives as
sensitive materials are found to explode more
rapidly at a given high temperature than less
sensitive ones.